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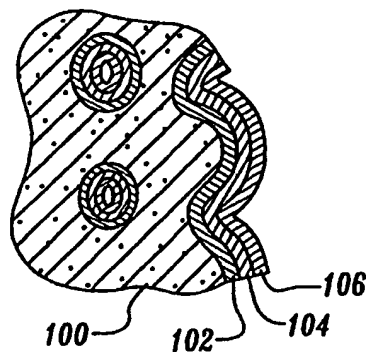
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US99/17083</p> <p>(22) International Filing Date: 27 July 1999 (27.07.99)</p> <p>(30) Priority Data: 09/123,781 27 July 1998 (27.07.98) US</p> <p>(71) Applicant: BATTELLE MEMORIAL INSTITUTE [US/US]; Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US).</p> <p>(72) Inventors: TONKOVICH, Anna, Lee, Y.; 1604 37th Place North, Pasco, WA 99301 (US). WANG, Yong; 2884 Troon Court, Richland, WA 99352 (US). GAO, Yufei; 302 North Hawaii, Kennewick, WA 99336 (US).</p> <p>(74) Agent: ZIMMERMAN, Paul, W.; Battelle Memorial Institute, Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, MSIN: K1-53, Richland, WA 99352 (US).</p>		<p>(81) Designated States: CA, JP, MX, NO, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i></p>

(54) Title: MULTILAYERED CATALYST AND METHOD FOR PREPARATION THEREOF

(57) Abstract

The present invention includes a catalyst that has at least four layers, (1) porous support, (2) buffer layer, (3) interfacial layer, and optionally (4) catalyst layer. The buffer layer provides a transition of thermal expansion coefficient from the porous support to the interfacial layer thereby reducing thermal expansion stress as the catalyst is heated to high operating temperatures. The method of the present invention for making the at least three layer catalyst has the steps of (1) selecting a porous support, (2) solution depositing an interfacial layer thereon, and optionally (3) depositing a catalyst material onto the interfacial layer; wherein the improvement comprises (4) depositing a buffer layer between the porous support and the interfacial layer.



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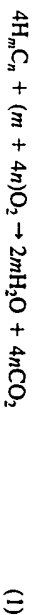
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Autocatalysts—Past, Present, and Future

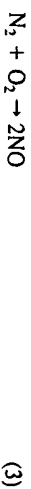
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1. INTRODUCTION

The development of the internal combustion engine, in the form of the gasoline spark-ignition engine used in automobiles, has provided society with tremendous mobility over recent decades. Indeed, the benefits to the individual are so strong that in many countries it can be said the car is a key component of modern society. The desired internal combustion reaction is the oxidation of hydrocarbon fuel to carbon dioxide and water, according to Eq. (1):



In practice, however, combustion is not completely efficient, and for this reason, as well as other physical effects, unburned hydrocarbons and partially combusted hydrocarbon oxygenates, such as aldehydes, may be present at varying levels in raw engine exhaust gas. In the pollution control arena these species are referred to differently in different parts of the world. The "hydrocarbons" are usually designated by the abbreviation HC. But in Europe, total hydrocarbons (THC), including the most difficult to oxidize, methane, are measured and reported; partially oxidized oxygenates are not measured. In America, methane is excluded, but oxygenates are included in nonmethane organic gases (NMOG) analysis. Carbon monoxide is also present as a partial oxidation product, which is formed according to Eq. (2). During the power stroke, moreover, under the conditions of high pressure and temperature, nitrogen and oxygen react in the engine cylinder and establish an equilibrium with nitric oxide, as in Eq. (3):



At some stage, as the product gases expand and cool rapidly en route to the exhaust system, this equilibrium is frozen, and although thermodynamically unstable at low temperatures, appreciable amounts (e.g., up to 3,500 ppm) of nitric oxide can be present in the exhaust gas from an engine.

The three major pollutants from the internal gasoline engine are HC, CO, and NO_x, and they are the cause of significant environmental concern. However, catalysts,

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MULTILAYERED CATALYST AND METHOD FOR PREPARATION THEREOF

5

FIELD OF THE INVENTION

The present invention relates to a catalyst useful for hydrocarbon
10 conversion and specifically to a catalyst structure that exhibits longer life
especially under high temperature conditions.

BACKGROUND OF THE INVENTION

15 Hydrogen and hydrocarbon conversion reactions including but not limited
to steam reforming, water-gas shift reactions, methanol synthesis and catalytic
combustion are well known. These reactions are usually carried out at
temperatures between 200 and 1000 °C. Currently these reactions are
industrially run using catalyst pellets which consist of an active catalytic metal or
20 metal oxide deposited on high surface area ceramic pellets.

Known foam or monolith catalysts are known to have three layers (1)
porous support, (2) interfacial layer, and (3) catalyst metal as described in [1]. In
making these catalysts, the interfacial layer has been deposited by various
methods including solution impregnation techniques. The catalyst layer may be
25 deposited by solution impregnation techniques. The interfacial layer has greater
surface area than the porous support whereas the porous support has greater
mechanical strength than the interfacial layer.

The porous support may be a metal or ceramic foam. Metal foams are
highly thermally conductive and easy to machine. The sponge-like mechanical
30 properties allow convenient sealing in a reaction chamber via mechanical
contact. The closely matched thermal expansion between the metal foam and
the housing reaction chamber minimizes cracking of the porous support and
minimizes gas channeling around the porous support at higher reaction
temperatures. Pestryakov *et al* prepared metal foam supported transition metal
35 oxide catalysts with [1] and without [2] an intermediate gamma-alumina layer for

the oxidation of n-butane. Kosak [3] examined several approaches to disperse precious metals on various metal foams where the surface was pre-etched with HCl solution, and reported that electroless deposition provides the best adhesion of precious metals to the foam supports. Podyacheva et al. [4] also synthesized foam metal supported LaCoO_3 perovskite catalyst with a porous alumina intermediate for methane oxidation. Despite all of the potential advantages with metal foam supported catalysts, metal foam has low corrosion resistance and its nonporous and smooth web surfaces have provided poor adhesion to ceramic materials.

In order to increase corrosion resistance, methods such as diffusion alloying with Al, Cr, and Si have been used to fabricate ferritic steels, which are typically used for the manufacturing of high temperature furnace elements (about 1200°C) [5]. When the aluminum containing ferritic steels are appropriately heat-treated, aluminum migrates to the alloy surface and forms a strongly adhering oxide film which is resistant to oxygen diffusion. Such ferritic steel foils have been used to fabricate metal monoliths with >10 ppi (pores per inch) open cells [6]. However, the search for the similar alloy foams with pores suitable for catalytic applications (<20ppi, 80ppi preferred) has been fruitless. This has been attributed to both the immature methods for making the finer Al-ferritic steel foams and the lack of the alloy precursors for making the foams.

Hence, there is a need in the art of supported catalysts for a porous support of a foam that is resistant to corrosion or oxidation and resists cracking of the interfacial layer.

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SUMMARY OF THE INVENTION

The present invention includes a catalyst that has at least three layers, (1) porous support, (2) buffer layer, (3) interfacial layer, and optionally (4) catalyst material. The buffer layer provides a transition of thermal expansion coefficient
10 from the porous support to the interfacial layer thereby reducing thermal expansion stress as the catalyst is heated to high operating temperatures. The buffer layer also reduces corrosion and oxidation of the porous support.

The method of the present invention for making the multi-layer catalyst (at least four layers) has the steps of (1) selecting a porous support, (2) solution
15 depositing an interfacial layer thereon, and optionally (3) depositing a catalyst material onto the interfacial layer; wherein the improvement comprises (4) depositing a buffer layer between the porous support and the interfacial layer.

The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both
20 the organization and method of operation, together with further advantages and objects thereof, may best be understood by reference to the following description taken in connection with accompanying drawings wherein like reference characters refer to like elements.

25

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an enlarged cross section of a catalyst.

FIG. 2 is a graph of weight gain (via oxidation) versus time.

30

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The catalyst of the present invention is depicted in **FIG. 1** having a porous
35 support **100**, a buffer layer **102**, an interfacial layer **104**, and, optionally, a catalyst layer **106**. Any layer may be continuous or discontinuous as in the form of spots or dots, or in the form of a layer with gaps or holes.

The porous support **100** may be a porous ceramic or a metal foam. The interfacial layer **104** is a solution deposited metal oxide. The solution deposited metal oxide includes but is not limited to γ - Al_2O_3 , SiO_2 , ZrO_2 , TiO_2 , magnesium oxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, nickel oxide, cobalt oxide, copper oxide, zinc oxide, molybdenum oxide, tin oxide, calcium oxide, aluminum oxide, lanthanum series oxide(s), zeolite(s) and combinations thereof. Typically the porous support **100** has a thermal coefficient of expansion different from that of the interfacial layer **104**. Accordingly, for high temperature catalysis ($T > 150^\circ\text{C}$) a buffer layer **102** is needed to transition between the two coefficients of thermal expansion. Another advantage of the buffer layer **102** is avoiding side reactions such as coking or cracking caused by a bare metal foam surface. For chemical reactions which do not require large surface area supports such as catalytic combustion, the buffer layer **102** stabilizes the catalyst metal due to strong metal to metal-oxide interaction. In chemical reactions which require large surface area supports, the buffer layer **102** provides stronger bonding to the high surface area interfacial layer **104**. The interfacial layer **104** may serve as a catalyst without any further catalyst layer deposited thereon.

The buffer layer **102** is a metal oxide that is Al_2O_3 , TiO_2 , SiO_2 , and ZrO_2 and combinations thereof. More specifically, the Al_2O_3 is α - Al_2O_3 , γ - Al_2O_3 and combinations thereof. The structure of the α - Al_2O_3 is preferred because TiO_2 is not as good as alumina against oxygen diffusion. Therefore, it is expected that resistance against high temperature oxidation can be improved with alumina coated on the porous support **100**. When the porous support **100** is metal foam, for example a stainless steel foam, a preferred embodiment has a buffer layer **102** formed of two sub-layers (not shown). The first sublayer (in contact with the porous support **100**) is TiO_2 for good adhesion and bonding of the ceramic layers to the porous support **100**. The second sublayer is α - Al_2O_3 which is used for passivating the metal foam and is placed upon the TiO_2 .

Deposition of the buffer layer **102** may be by vapor deposition including but not limited to chemical vapor deposition, physical vapor deposition or combinations thereof. Because the vapor deposition is conducted at high temperatures, polycrystalline phases are formed providing good adhesion of the

metal oxide to the metal foam surface. Alternatively, the buffer layer **102** may be obtained by solution coating. For example, the solution coating has the steps of metal surface functionalization via hydroxide formation, followed by surface hydrolysis of alkoxides to obtain the polycrystalline phases. This solution coating
5 may be preferred as a lower cost method of depositing the buffer layer **102**. Polycrystalline metal oxides resist flaking of layers after several thermal cycles.

Because metal foam has web surfaces that are nonporous and smooth, deposition of the interfacial layer may be impeded. One way to mitigate this problem is to rough the metal foam surface via chemical etching. The adhesion
10 of high surface area gamma-alumina supported metal catalysts to metal foam is significantly improved when metal foam is roughed via chemical etching using mineral acid solutions, for example HCl. Roughed web surface also shows improved resistance to the spalling of catalyst layer under thermal cyclings. The open cells of a metal foam may range from about 20 ppi to about 1000 ppi and is
15 preferably about 80 ppi.

The catalyst layer **106** (when used) is deposited onto the interfacial layer **104**. The catalyst layer may be any catalyst metal including but not limited to noble metal, transition metal and combinations thereof, or a catalyst metal oxide
20 or transition metal oxide including but not limited to magnesium oxide, titanium oxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, nickel oxide, cobalt oxide, copper oxide, zinc oxide, zirconium oxide, molybdenum oxide, tin oxide, calcium oxide, aluminum oxide, silicon oxide, lanthanum series
oxide(s), zeolite(s) and combinations thereof.

The method of making the catalyst has the steps of selecting a porous
25 support **100**, and solution depositing an interfacial layer **104** thereon; wherein the improvement is obtained by depositing a buffer layer **102** between the porous support **100** and the interfacial layer **104**. In a preferred embodiment, wherein a metal foam is used as the porous support **100**, the metal foam is etched prior to vapor depositing the buffer layer **102**. Etching is preferably with an acid, for
30 example HCl. Optionally a catalyst layer **106** may be deposited onto the interfacial layer **104**.

Example 1

An experiment was conducted to demonstrate the catalyst layer of the present invention.

5 A stainless steel foam was coated with 1000 Angstroms TiO_2 via chemical vapor deposition. SEM (scanning electron microscope) analysis showed that the stainless steel foam supported gamma-alumina with a TiO_2 buffer layer did not show spalling after several (3) thermal cycles from room temperature to 600 °C. In a control experiment with a stainless steel foam support coated with gamma-alumina without the TiO_2 buffer layer, severe flaking or spalling of the gamma
10 alumina under the identical testing conditions was observed. Resistance to high temperature oxidation is shown in FIG. 2

CLOSURE

15 While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

CLAIMS

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We claim:

1. A catalyst comprising a porous support having an interfacial layer thereon; wherein the improvement comprises a buffer layer between the porous support and the interfacial layer.

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2. The catalyst as recited in claim 1, further comprising a catalyst layer upon the interfacial layer.

15

3. The catalyst as recited in claim 1, wherein said porous support is a metal foam.

4. The catalyst as recited in claim 1, wherein said porous support is a porous ceramic.

20

5. The catalyst as recited in claim 1, wherein said interfacial layer is a solution deposited metal oxide.

25

6. The catalyst as recited in claim 5, wherein said solution deposited metal oxide is selected from the group consisting of γ - Al_2O_3 , SiO_2 , ZrO_2 , TiO_2 , magnesium oxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, nickel oxide, cobalt oxide, copper oxide, zinc oxide, molybdenum oxide, tin oxide, calcium oxide, aluminum oxide, lanthanum series oxide(s), zeolite(s) and combinations thereof.

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7. The catalyst as recited in claim 2, wherein said catalyst layer is a metal selected from the group of noble metal, transition metal and combinations thereof.

8. The catalyst as recited in claim 2, wherein said catalyst layer is a metal oxide or transition metal oxide selected from the group consisting of magnesium oxide, titanium oxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, nickel oxide, cobalt oxide, copper oxide, zinc oxide, zirconium oxide, molybdenum oxide, tin oxide, calcium oxide, aluminum oxide, silicon oxide, lanthanum series oxide(s), zeolite(s) and combinations thereof.

9. The catalyst as recited in claim 1, wherein said buffer layer is a metal oxide.

10

10. The catalyst as recited in claim 9, wherein said metal oxide is selected from the group of Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 and combinations thereof.

11. The catalyst as recited in claim 9, wherein said Al_2O_3 is selected from the group consisting of $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ and combinations thereof.

15

12. The catalyst as recited in claim 1 wherein said buffer layer comprises a plurality of sublayers.

20

13. A method of making a catalyst comprising the steps of selecting a porous support, solution depositing a interfacial layer thereon, wherein the improvement comprises depositing a buffer layer between the porous support and the interfacial layer.

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14. The method as recited in claim 13, further comprising depositing a catalyst layer onto the interfacial layer.

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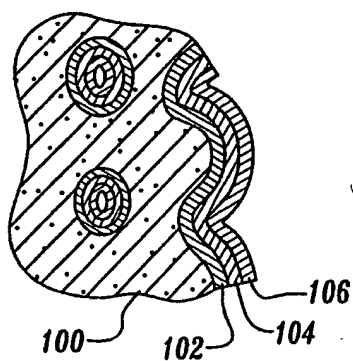
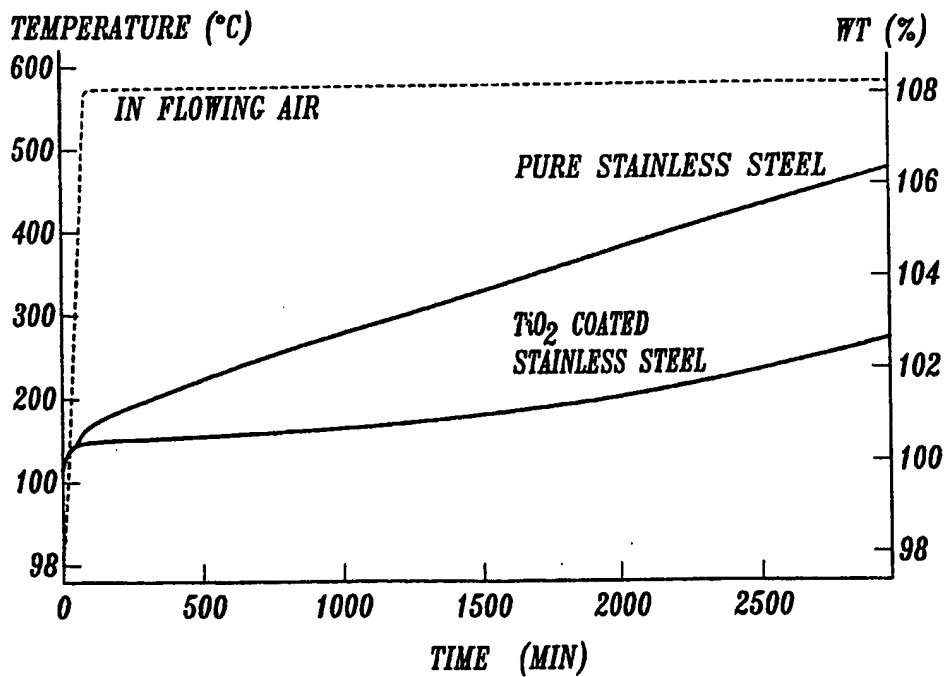
15. The method as recited in claim 13, wherein said buffer layer is a metal oxide.

16. The method as recited in claim 15, wherein said metal oxide is selected from the group consisting of Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 and combinations thereof.

17. The method as recited in claim 15, wherein said Al_2O_3 is selected from the group consisting of $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ and combinations thereof.

5 18. The method as recited in claim 13, wherein depositing the buffer layer is by vapor deposition.

19. The method as recited in claim 13, wherein depositing the buffer layer is by solution deposition.

*Fig. 1**Fig. 2*

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/17083

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J37/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 574 012 A (SHIMADZU CORP) 15 December 1993 (1993-12-15)	1,2,4-7, 9,10, 13-16,18 3,11,17
A	column 8, line 14 -column 9, line 36 column 10, line 2 - line 32 ---	
X	DATABASE WPI Section Ch, Week 199824 Derwent Publications Ltd., London, GB; Class E36, AN 1998-270052 XP002118724 & RU 2 093 261 C (BELO KIROV TECHN INST), 20 October 1997 (1997-10-20) abstract --- -/--	1,3,5,6, 9-11,13, 15-17



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 5 690 900 A (SMOJVER RADMIL) 25 November 1997 (1997-11-25) examples 1-3 -----	1,2,4-7, 9,10, 13-16,19
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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